



# On the redox nature of ceria-zirconia mixed nanocatalysts and its effect on catalytic wet peroxide oxidation of chlorinated organic pollutants



Christy Kunjachan, Asha Sreevalsan, Manju Kurian\*

Department of Chemistry, Mar Athanasius College, Kothamangalam, 686666, India

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## ABSTRACT

The potential application of  $Zr_xCe_{1-x}O_2$  ( $x$ : 1, 0.75, 0.5, 0.25, 0) nanocomposites in the oxidation of chlorinated phenolic compounds was studied with respect to Catalytic Wet Peroxide oxidation of 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4-dichlorophenoxy acetic acid (2,4-D) was experimented in presence of aqueous hydrogen peroxide as oxidant. Zirconium doping on nanoceria lattice increased its catalytic activity towards Wet Peroxide Oxidation of the target pollutants. 4-CP (500 mg/L) was degraded with 14.9% TOC and 45.8% COD removal after 75 min at 70 °C using  $Zr_{0.75}Ce_{0.25}O_2$  catalyst. 2,4-DCP (250 mg/L) conversion with 22.5% TOC and 52.8% COD removal was observed at 75 min over  $Zr_{0.5}Ce_{0.5}O_2$  catalyst. 100% catalytic oxidative conversion of 2,4-D (250 mg/L) with 23.68% Total Organic Carbon (TOC) and 47.80% Chemical Oxygen Demand (COD) removal was achieved at 70 °C at 90 min. Temperature Programmed Reduction (TPR) analysis indicated that the reducing capacity of ceria increased on zirconium doping. The catalysts were stable and reusable upto six successive runs as demonstrated by X-ray diffraction (XRD) and surface area measurements.

## 1. Introduction

Intensive use of pesticides in agricultural practice has brought out environmental and health concerns since it impacts water and soil quality negatively [1–4]. Due to its non-biodegradable occurrence in water bodies, World Health Organization (WHO) refers it as moderately toxic [5]. Chlorophenols like 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) are priority pollutants and is commonly used as a wood-preservative agent, pesticide, insecticide, and defoliant. It can be found in chlorine-disinfected drinking water, river water, landfill leachate, chemical plant effluent, sewage treatment plant effluent, and fish exposed to pesticide run-off [6,7]. 2,4-dichlorophenoxyacetic acid (2,4-D) is one of the most used phenoxy alkanolic herbicides in world, and more than 1500 pesticides contain 2,4-D as active substance. Phenoxyalkanoic herbicides are considered as serious contaminants of streams, lakes and rivers, especially because of their high solubility in water and low tendency to accumulate in organic matter. As a matter of fact, 2,4-D has frequently been detected in surface and ground waters. Moreover, 2,4-D is known to present serious ecological impact, like toxic effects on birds, beneficial insects, non-target plants but also on algae, small invertebrates, amphibians, fishes and more generally on aquatic life [8–11].

Nowadays much research has been devoted to identify environmental problems using nanoscience and technology. As a result,

different approaches have been extended to offer new ways to prevent or pre-treat highly toxic and persistent organic pollutants. Concepts of green chemistry and process sustainability have become issues of global importance for industries. Meanwhile, more efficient and economic solutions for end-stream treatment, avoiding high-energy input technologies are imperative to produce reusable process water and environmentally friendly effluents [12,13]. Over the past few decades, literature discloses various studies focusing on removal of chlorophenols and 2,4-D using ozonation [14–16] processes, advanced oxidation processes (AOPs) like electrochemical degradation [17], Fenton and Fenton-like processes [18,19], photocatalysis [20,21] and combination of AOPs with biological treatment [22,23]. Despite their efficiency, total mineralization of effluents can be time and energy-consuming, thus increasing operational costs. These processes show other drawbacks such as disposal of residuals [24]. AOP like catalytic degradation using  $H_2O_2$  as oxidant appears as a good alternative to reduce operating costs [25,26]. The simultaneous generation of hydroxyl and organic radicals initiates chain reactions leading to oxidation of organic substrates in aqueous phase. Hydroxyl radical is a transient species with high reactivity towards a wide variety of undesirable organics, such as phenol, cresol, chlorophenol, dichlorophenol, trichlorophenol and benzene [27,28].

In this context we developed a simplified method for abatement of non-biodegradable organic wastewater pollutants using  $Zr_xCe_{1-x}O_2$  ( $x$ :

\* Corresponding author.

E-mail address: [mk@macollege.in](mailto:mk@macollege.in) (M. Kurian).

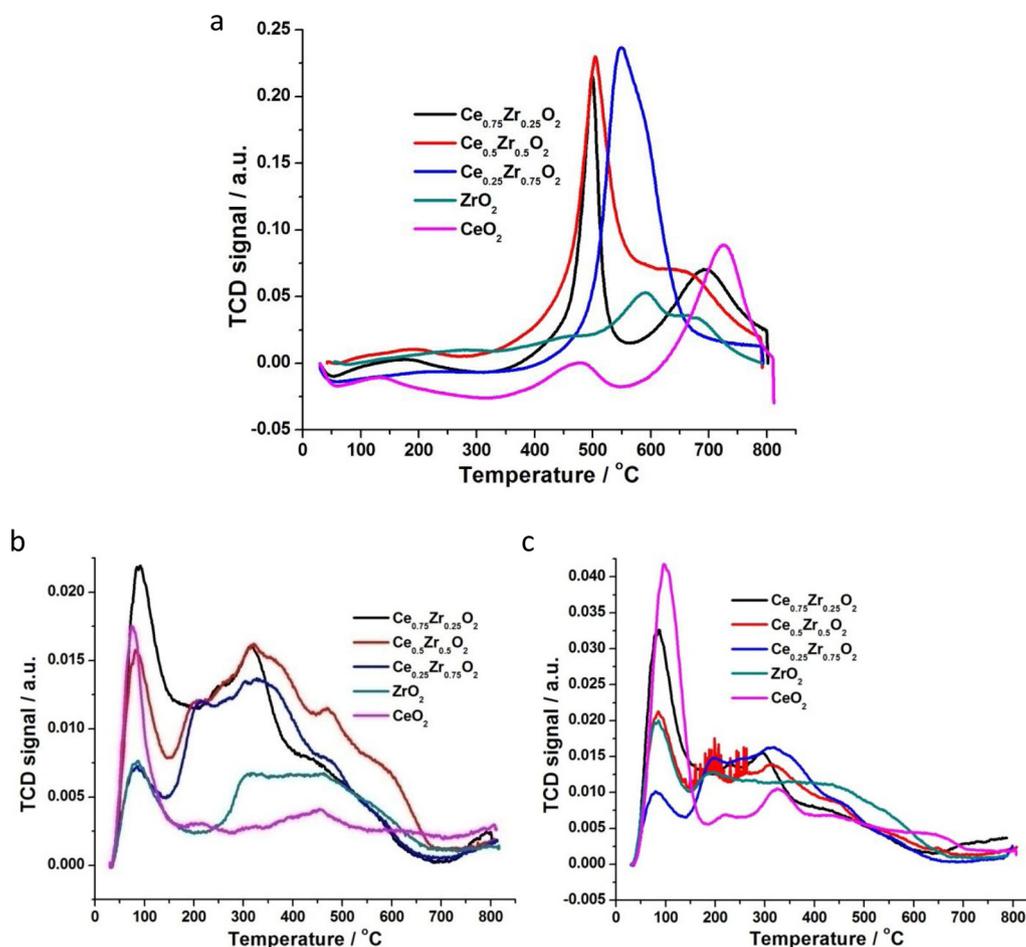


Fig. 1. (a) TPR profile of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $x$ : 1, 0.75, 0.5, 0.25, 0). (b)  $\text{NH}_3$ -TPD profile of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $x$ : 1, 0.75, 0.5, 0.25, 0) (c)  $\text{CO}_2$ -TPD profile of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $x$ : 1, 0.75, 0.5, 0.25, 0).

1, 0.75, 0.5, 0.25, 0) nanocatalysts by wet oxidative degradation of 4-CP, 2,4-DCP and 2,4-D. Zirconium doped cerium oxide is an attractive material for AOPs due to its redox properties. Doping with metal ions having lower valence and/or small size into ceria lattice improves its redox performance [28–30]. Our objectives were to study the structural stability, reusability and the ease of recovery of spent catalysts from the reaction mixture. Effect of different reaction variables on reaction rate was also studied and a suitable kinetic model and mechanism has been arrived at in the present study. Reusability of catalysts was studied by structural examination of catalyst surface by XRD and surface area measurements.

## 2. Materials and methods

$\text{Zr}_x\text{Ce}_{1-x}\text{O}_2$  ( $x$ : 1, 0.75, 0.5, 0.25, 0) nanocatalysts were prepared by coprecipitation method using cerium(III) nitrate hexahydrate and zirconium(IV) oxynitrate precursors. The procedure for coprecipitation was opted according to our previous work [30,31]. Temperature Programmed Reduction experiments were performed in a Micromeritics TPx system using 10%  $\text{H}_2$  in Helium flowing at 5 ml/min. Total acidity was evaluated by temperature-programmed desorption of ammonia/carbon dioxide using a Micromeritics TPx system. Catalytic activity experiments were performed by placing the reaction mixture containing 50 ml of 500 mg/L 4-CP/250 mg/L 2,4-DCP/250 mg/L 2,4-D solutions, 500 mg/L catalyst and requisite amounts of hydrogen peroxide in a 100 ml round bottom flask connected to a condenser and agitating with a magnetic stirrer. At specific intervals, aqueous sample was withdrawn and filtered immediately by Whatman grade1 filter paper. The samples

were quantitatively analysed using Perkin Elmer Clarus 580 Gas Chromatograph equipped with an Elite-5 capillary column and expressed as percentage conversion of 4-CP, 2,4-DCP and 2,4-D. Extent of oxidation and total organic carbon removal was measured using COD measurements with standard dichromate method and Shimadzu TOC-L analyzer respectively. Removal percentage of chemical oxygen demand (COD) was calculated as  $\{[\text{COD}]_0 - [\text{COD}]_t\} / [\text{COD}]_0 \times 100$  where  $[\text{COD}]_0$  and  $[\text{COD}]_t$  are CODs at initial and at time  $t$  respectively. Residual amount of peroxide was back calculated by dichrometry. All experiments were repeated twice and averages are reported. X-ray diffractograms of reused catalysts were recorded on a Rigaku MiniFlex 600 X-ray diffractometer using  $\text{CuK}\alpha$  radiation. Phase identification was carried out by comparison with JCPDS database cards and average crystallite size was determined by Scherrer equation. Specific surface area measurements were done by nitrogen physisorption at 77 K using a Micromeritics Gemini VII instrument according to standard Brunauer-Emmett-Teller (BET) procedure.

## 3. Results and discussions

### 3.1. Catalyst characterisation

A detailed characterization of the prepared Ce-Zr nano oxides was presented in our previous publication [30] and is summarized in forthcoming discussion. X-ray diffractogram peaks of  $\text{Zr}_x\text{Ce}_{1-x}\text{O}_2$  can be indexed to cubic fluorite structure of ceria, when Zr content is upto 0.5. Increased concentrations of Zr broaden and shift the peaks indicating transformation from cubic to a mixed phase. XRD pattern of zirconia

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